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Oxygen Reduction on Polycrystalline Pt and Au Electrodes in Perchloric Acid Solution in the Presence of Acetonitrile

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Oxygen reduction reaction (ORR) was studied on polycrystalline Pt and Au electrodes in 0.1 M $HClO_4$ solutions containing various amounts of acetonitrile (AcN). The state of the electrode surface was characterized by cyclic voltammetry in oxygen free electrolytes, while ORR studies were performed on polycrystalline Pt and Au rotating disc electrodes by a linear sweep voltammetry in oxygen saturated electrolytes. Acetonitrile is chemisorbed on Pt over a wide potential range inhibiting both H adsorption and oxide formation. The extent of AcN chemisorption depends on its concentration in the solution. Initial potential of oxygen reduction is shifted negatively, while the kinetics of ORR is increasingly hindered with the increase of AcN concentration. Inhibiting effect of acetonitrile on ORR is pronounced on both Pt(poly) and Au(poly). Complete inhibition of ORR in the potential range of AcN chemisorptions is achieved for 0.1 M $HClO_4$ solution containing 1 M AcN on Au(poly) and 3 M AcN on Pt(poly).

Keywords: Oxygen reduction, platinum, gold, acetonitrile, perchloric acid, rotating disc electrode

1. INTRODUCTION

The chemisorption of acetonitrile (AcN) on metal surfaces provides interesting systems in electrochemical surface science for a comprehensive examination of chemisorption and surface reactivity of such modified electrodes, which include studies with the addition of increasing amounts of AcN in various aqueous solutions as well as studies in pure aprotic AcN solution.

Since the reactivity of chemically modified metal surfaces is significantly different than the reactivity of pure metals, we have chosen to investigate how oxygen reduction reaction (ORR) on both Pt(poly) and Au(poly) is affected by the adsorption of acetonitrile. The aim was to study the kinetics of ORR itself and additionally to get a feedback about the adsorption of AcN on these surfaces.

After an earlier work on the chemisorption of acetonitrile on polycrystalline platinum, Pt(poly), which provided "the first chemically modified electrode" [1], the adsorption behavior and stability of acetonitrile was widely studied on Pt(poly) and on single crystal platinum electrodes in various solutions using different electrochemical and spectroscopic techniques [2-10]. Following controversial reports on the stability of adsorbed acetonitrile with potential [11, 12], in the most recent systematic study on its adsorption on platinum electrodes in acidic sulfate solutions [13], it was confirmed that there was no electrochemical conversion of AcN at $E < 1.0$ V (vs. SHE) on well–defined Pt single crystals, while at higher potentials the oxidation of AcN on Pt(poly) proceeded simultaneously with the product desorption. Besides, it was observed that AcN molecules are adsorbed on the surface of platinum electrodes in the potential range of 0.03–0.9 V (vs. SHE), blocking the adsorption sites for hydrogen adatoms and shifting the region of (bi)sulphate anion adsorption/desorption to higher potentials.

Acetonitrile adsorption was also investigated on polycrystalline gold electrodes, Au(poly), although in a lesser extent. The study of the acetonitrile adsorption on Au(poly) in perchloric acid solution by *in situ* vibrational spectroscopy [14] has shown that two types of acetonitrile molecules existed at the interface. The first one involved chemisorbed AcN molecule with its dipole vector perpendicular to the interface and with its negative end attached directly to the surface. The second one involved acetonitrile molecules hydrogen bonded to chemisorbed water molecules and thus located further away from the surface. Besides, in the same study no evidence of perchlorate anions contact adsorption was found. In a recent study of AcN adsorption on gold nanorods by non-resonant Raman measurements and density functional theory calculations [15], it was proposed that AcN molecules were chemisorbed on the Au nanostructure in the form of $[\mathrm{AcN} + 2\mathrm{Au}]^0$. Most recently, it was reported [13] that AcN adsorbs much weaker on the Au(111) than on the Pt(111) surface from acidic sulphate solution, with its total desorption at potentials higher than 0.9 V (vs. SHE).

Earlier rotating disc electrode (RDE) studies of oxygen reduction in aprotic acetonitrile solution on graphite [16] as well as on Pt(poly), [17,18] have shown that the first step is a reversible one and occurs with the exchange of one electron giving superoxide anion as a product. Superoxide anion is stable in the absence of proton sources, but with the addition of water or proton to the aprotic AcN solution, the ORR occurs with a further charge transfer resembling the pathways observed for acid or alkaline solutions [17-19].

In this work, the effect of AcN adsorption alone on ORR on both Pt(poly) and Au(poly) was studied in acid solutions containing perchlorate anions which are known to adsorb weakly on both surfaces examined, and containing AcN in a wide range of concentrations.

2. EXPERIMENTAL

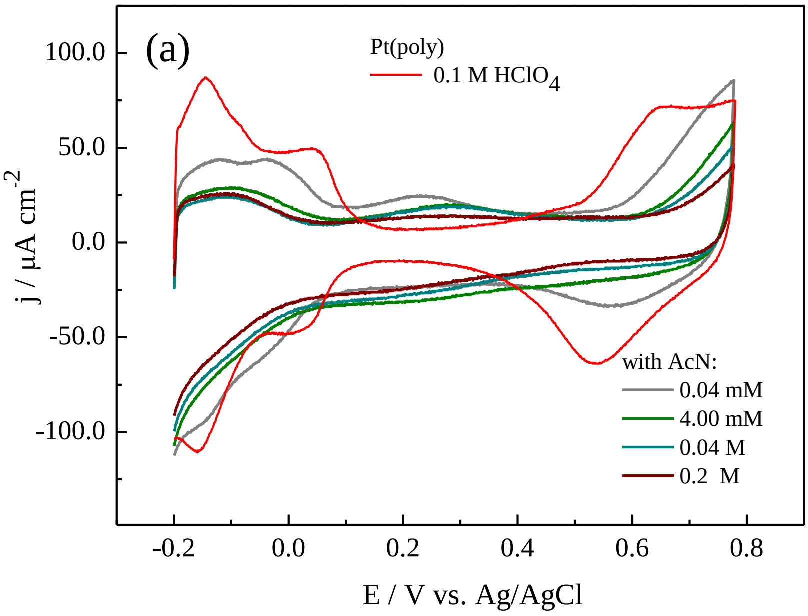
Polycrystalline Pt and Au rotating disc electrode, 5 mm in diameter, mounted in modulated speed rotator (Pine Instruments Co.) were used as working electrodes. The state of the electrode surface was checked by cyclic voltammetry (CV), while oxygen reduction measurements were performed by a linear sweep voltammetry (LSV). The carrying electrolyte was 0.1 M $HClO_4$, while the concentration of acetonitrile in solution varied from 0.04 mM to 3 M. All LSV curves are recorded while scanning the potential in the negative direction. Before each experiment, the preparation of the Pt and Au electrode surfaces consisted of the electrochemical polishing and of the potential cycling in deaerated solutions in the potential range within hydrogen and oxygen evolution reactions until clean and stable CV curves were obtained.

The solutions were prepared from pure $HClO_4$ (Merck), acetonitrile (HPLC grade) and Milli-pure water. CV measurements were performed in solutions deaerated by N_2 (99,999%, Messer), while LSV measurements were performed in O_2 (99,999%, Messer) saturated solutions. The counter electrode was Pt wire and the reference electrode was Ag/AgCl, 3M KCl. All measurements were performed at room temperature (23 ± 2 ^{o}C).

3. RESULTS AND DISCUSSION

3.1. Acetonitrile adsorption on Pt(poly) in 0.1 M $HClO_4$ - Cyclic voltammetry measurements

Cyclic voltammograms (CVs) of a Pt(poly) electrode in oxygen free pure 0.1 M $HClO_4$ solution and in ones with the addition of 0.04 mM – 3 M of acetonitrile are presented in Figure1. It is well known that $HClO_4^-$ anions are only weakly (nonspecifically) adsorbed on the platinum surface and therefore their presence in the electrolyte does not affect the other electrochemical processes including hydrogen and OH adsorption/desorption and oxide formation/reduction reactions [20,21]. A typical CV profile of polycrystalline Pt in pure perchloric acid solution, Figure 1 (a) (red curve), shows two pairs of peaks corresponding to adsorbed hydrogen which appear in both scan directions at -0.13 V and -0.02 V, respectively. At potentials higher than 0.5 V, OH adsorption takes place, which is followed by a gradual PtO formation with increasing potential to the more positive values. Effect of the addition of acetonitrile on CV profiles is clearly seen in Figure 1 (a) for lower AcN concentrations in the range from 0.02 mM to 0.2 M, and in Figure 1 (b), for higher (AcN) concentrations (1-3 M).



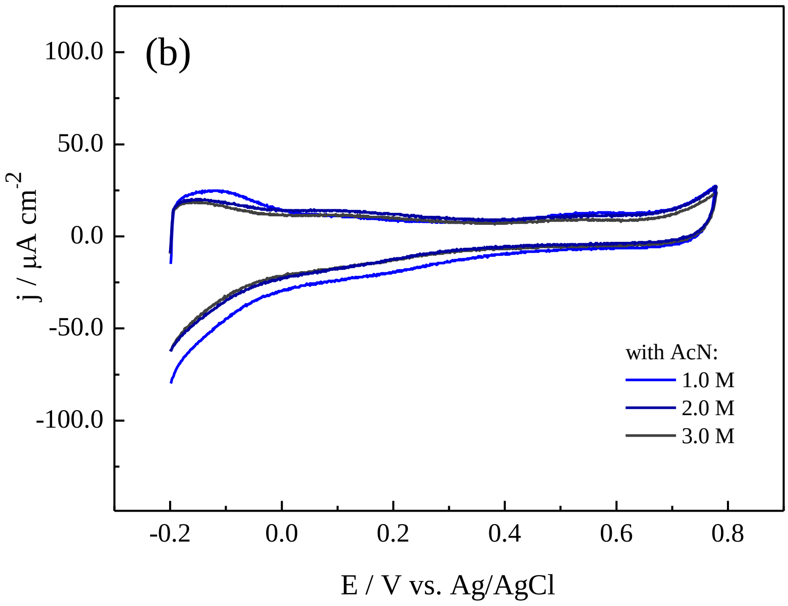


Figure 1. CVs of a Pt(poly) electrode recorded in oxygen free 0.1 M $HClO_4$ solution: (a) without and with the addition of 0.04 mM – 0.2 M of AcN; (b) with the addition of 1.0 M – 3.0 M of AcN. Potential scan rate was 50 mV/s.

For lower concentration of acetonitrile, both hydrogen adsorption/desorption and PtOH oxidation/reduction peaks are being increasingly suppressed with the increase of AcN concentration indicating that the adsorption of AcN competes with the adsorption of hydrogen and OH anions. Double layer expands with the addition of very small amount of acetonitrile (0.04 mM), but with the increase of its concentration, double layer narrows although generally staying wider than the double layer of Pt(poly) in pure perchloric acid solution. These changes in CVs profiles indicate that acetonitrile adsorption occurs in the whole potential region investigated.

3.2. Oxygen reduction on Pt(poly) in 0.1 M $HClO_4$ containing acetonitrile - Rotating disc electrode measurements

Linear sweep voltammetry curves for ORR on Pt(poly) in pure 0.1 M $HClO_4$ solution and in ones with the addition of the increasing amount of AcN are presented in Figure 2 for the same rotation rate of 1600 rpm. The initial potential for ORR in pure 0.1 M $HClO_4$ is (700 ± 10) mV and falls within the double layer potential region. Since, the PtOH formation takes place at potentials higher than 0.4 V its relevance for ORR will be discussed below. In the presence of acetonitrile in concentrations of 0.04 mM, 4 mM, 0.04 M and 0.2 M and 1 M, the initial potential for oxygen reduction shifts to 650 mV, 620 mV, 590 mV and 550 mV, respectively. For AcN concentrations of 1 M and higher the initial potential shifts to 420 mM and below.

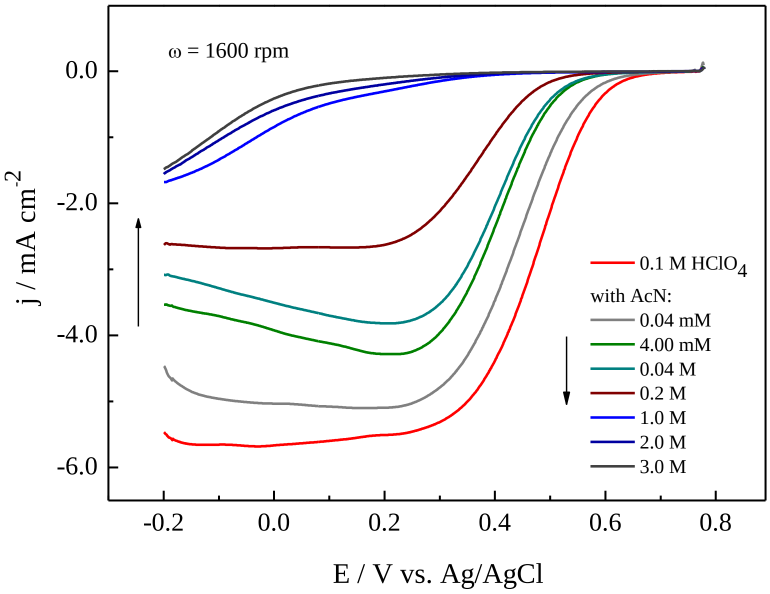


Figure 2. LVs for ORR on a rotating Pt(poly) electrode in oxygen saturated 0.1 M $HClO_4$ solution without and with the addition of 0.04 mM – 3 M of acetonitrile, obtained for the same rotation rate of 1600 rpm. Potential scan rate was 50 mV/s. Arrows indicate directions in which the current density decreases with the increase of AcN concentration.

LSV curves for ORR on Pt(poly) in pure 0.1 M $HClO_4$ solution and, as an illustration, in one containing 0.2 M of AcN, recorded for six rotation rates and corresponding Koutecky–Levich plots are presented in Figure 3.

According to Koutecky–Levich theory, the measured current, j, is given by:

$$1/j = 1/j_k + 1/j_l \qquad (1)$$

where, j_k is the kinetic current and j_l is the diffusion limiting current, or:

$$1/j = 1/j_k + 1/B\omega^{1/2}, \qquad (2)$$

where the measured current density is expressed as a function of the rotation rate.

$$B = 0.62nFC_{O2}D_{O2}^{2/3}\nu^{-1/6}, \qquad (3)$$

where n is the overall number of electrons exchanged, F is Faraday's constant, D_{O2} is oxygen diffusivity, ν is the kinematics' viscosity of the electrolyte.

Koutecky–Levich plots are obtained when the inverse current density (1/j) is plotted as a function of the inverse of the square root of the rotation rate ($\omega^{-1/2}$). From equation 1, the kinetic current can be expressed as:

$$j_k = j/(1-j/j_l). \qquad (4)$$

Tafel plot defined as a function of the gradient of the potential vs. kinetic current gradient ($\Delta E/\Delta \log j_k$) is obtained by plotting E vs. $\log j_k$, where j_k is taken as the average value for six rotation rates.

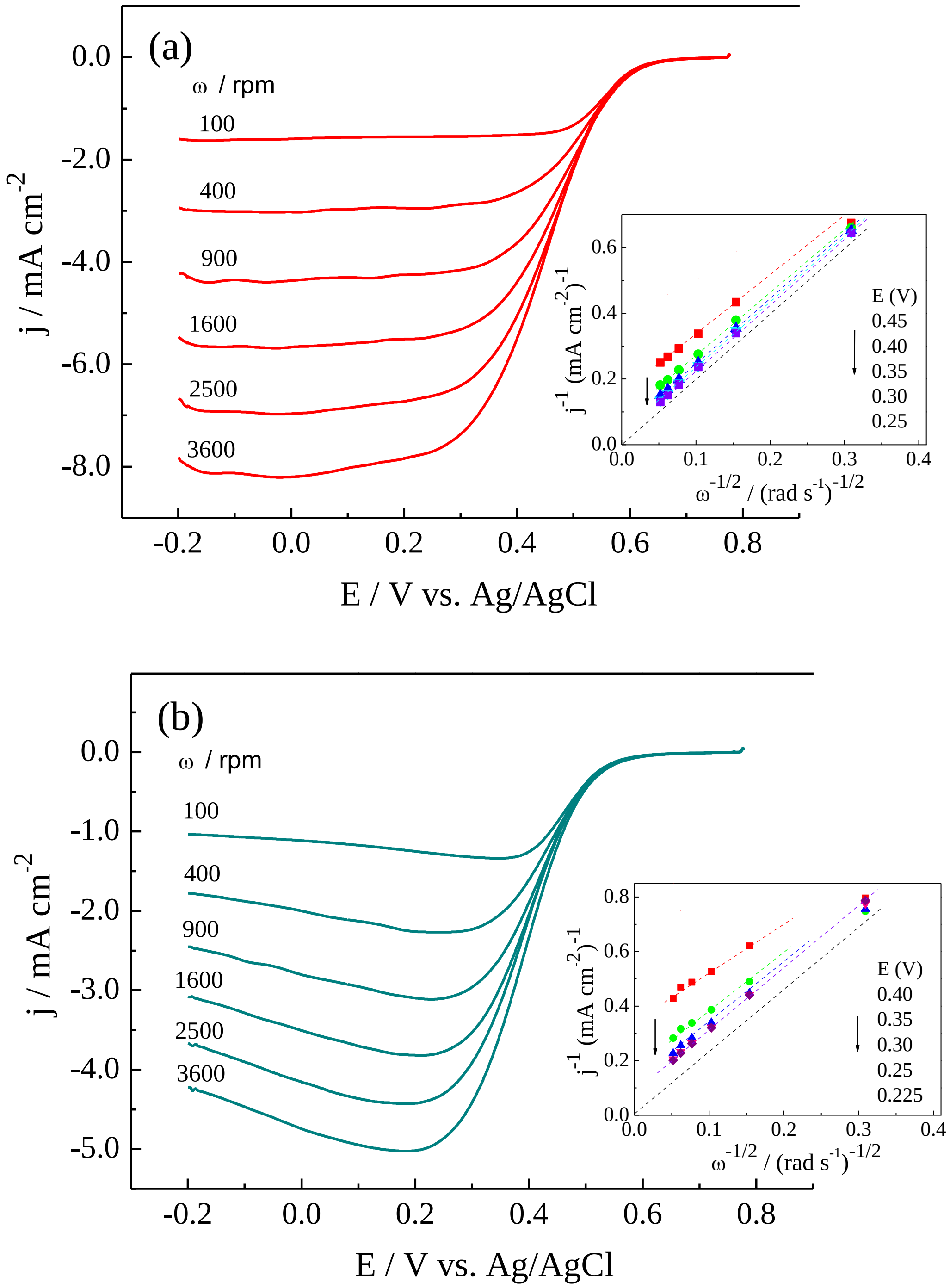


Figure 3. LVs for ORR on a rotating Pt electrode in oxygen saturated 0.1 M $HClO_4$ solution: (a) without and (b) with 0.2 M AcN. LVs were obtained for various rotation rates with the potential scan rate of 50 mV/s. Inserts: the corresponding Koutecky–Levich plots.

The linearity and parallelism of Koutecky–Levich plots for ORR in pure 0.1 M $HClO_4$ solution and in one containing AcN in the lowest concentration of 0.04 mM (not presented due to apparent similarity), Figure 3 (a), indicate the first–order kinetics with respect to molecular oxygen. On the other hand, for higher AcN concentrations both linearity and parallelism of these plots are slightly altered, while the apparent disturbance can be seen for AcN concentration as high as 0.2 M, Figure 3 (b), indicating a significant change in reaction kinetics. This occurs most likely due to the occupation of a number of Pt sites by adsorbed AcN, which consequently leads to a significant decrease of the amount of adsorbed oxygen as a reactant. Besides, there are also some changes of oxygen solubility, oxygen diffusivity and kinematics' viscosity of the electrolyte due to the presence of a larger amount of acetonitrile. Therefore, the first order reaction kinetics with respect to dissolved oxygen can be evaluated from these plots for AcN concentration lower than 0.2 M.

This is in accordance with previous rotating disc electrode studies of oxygen reduction in aprotic acetonitrile solution on Pt(poly), [17,18], where it was shown that the first step is a reversible one and occurs with the exchange of one electron giving superoxide anion as a product.

$$O_2 + e \leftrightarrow O_2^- \qquad (5)$$

Superoxide anion is stable in the absence of proton sources and undergoes disproportionation according to the reaction:

$$2O_2^- \rightarrow O_2 + O_2^{2-} \qquad (6)$$

With the addition of water or proton to the aprotic AcN solution, the ORR occurs with a further charge transfer resembling the pathways observed for acid or alkaline solutions [17–19]. Detection of superoxide anion by surface-enhanced infrared reflection absorption spectroscopy during ORR on Pt in pure aqueous solutions [22] was a final proof that the exchange of the first electron is the first reaction step. This reaction kinetics can also be challenged by the estimation of the slope of the Tafel plots in this case, where starting from pure perchloric acid the increasing amounts of AcN are added into the solution.

Tafel plots obtained from the data taken from LSV curves for six rotation rates, for AcN concentrations of 0.04 mM up to 0.2 M, are presented in Figure 4. It is well known that the Tafel slope for ORR on Pt electrodes in perchloric acid solution is -60 mV/dec at higher potentials i.e., in the kinetic control region, due to the partial coverage of the Pt surface with adsorbed OH species [23, 24]. The same is obtained here only for pure perchloric acid. The fact that this slope is not found even in the case where the smallest amount of acetonitrile is added into the solution indicates that the OH formation on Pt(poly) is inhibited enough and that ORR occurs predominantly on an oxide free surface. Experimentally found as well as calculated value of the intrinsic Tafel slope of -120 mV per decade is a criterion that the exchange of the first electron is the rate determining step during ORR on Pt in both acid and alkaline solutions [24–26]. Since in the presence of acetonitrile, the Tafel slopes have the value of -120 mV per decade for AcN concentrations up to 0.2 M, this confirmed that the first step in these cases occurs according to reaction (5) on oxide free surface sites.

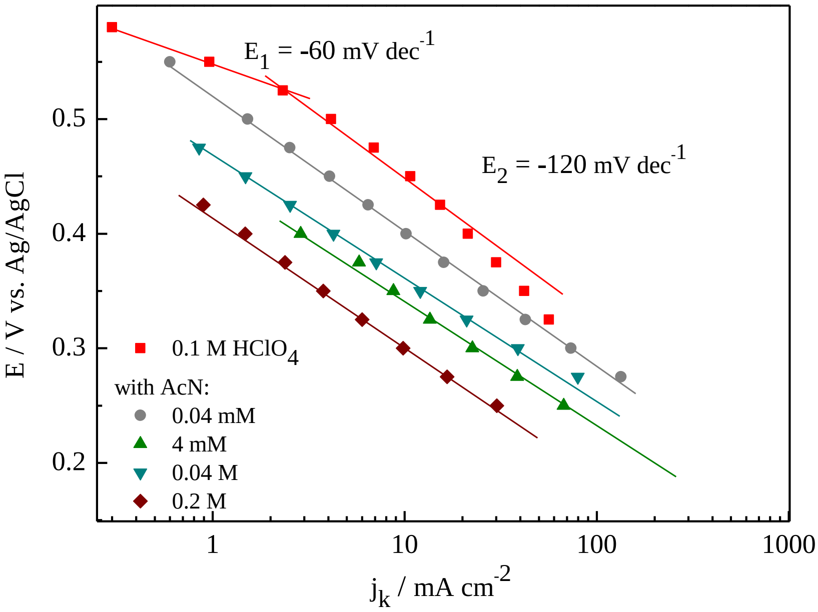
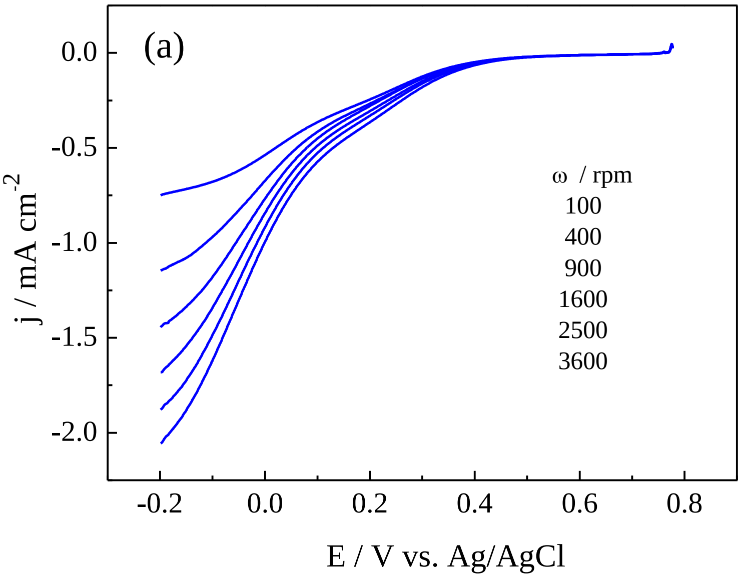


Figure 4. Tafel plots for ORR on Pt(poly) in 0.1 M $HClO_4$ solution and in ones containing 0.04 mM – 0.2 M of AcN. Plots are obtained from the data from Fig.3 and from (not presented) related data taking the average value of j_k for six rotation rates.

LSV curves for ORR on Pt(poly) in 0.1 M $HClO_4$ solution containing AcN in concentrations of 1 M and 2 M, recorded for six rotation rates, are presented in Figure 5. One can see from Figure 5 (a) that for AcN concentration of 1 M, a proper diffusion control is not established and that the ORR is significantly blocked which enables any kinetic analysis. For AcN concentration of 2 M and higher, Figure 5 (b), ORR is almost completely blocked in the whole potential region of AcN adsorption.

In the negative going sweep, the negative potential limit where ORR begins is indicative of the beginning of AcN desorption for this particular solution. This can be determined for any other solution, by increasing the AcN concentration up to the complete ORR inhibition.



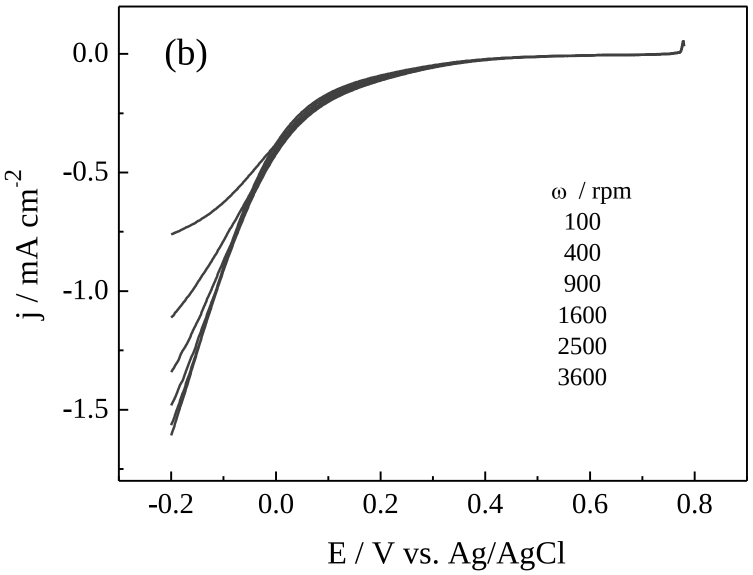


Figure 5. LVs for ORR on a rotating Pt(poly) electrode in oxygen saturated 0.1 M $HClO_4$ solution with the addition of: (a) 1.0 M AcN; (b) 3.0 M AcN obtained for various rotation rates with the potential scan rate of 50 mV/s.

3.3. Oxygen reduction on Au(poly) in 0.1 M $HClO_4$ solutions containing acetonitrile

CVs for a Au(poly) electrode recorded in oxygen free pure 0.1 M $HClO_4$ solution and in ones with the addition of 4.0 mM, 0.2 M and 1 M of acetonitrile are presented in Figure 6 (a). Since there is no adsorption of hydrogen like in the case of Pt electrode surface, the only indication of AcN adsorption in the potential region relevant for ORR studies in the solution containing weakly adsorbed perchlorate anions, is the change in the double layer. One can see that the double layer slightly narrows with the increase of acetonitrile concentration. Apart from that no other significant changes in CVs can be attributed with certainty to the acetonitrile adsorption. On the other hand, ORR appeared to be much more sensitive to the AcN adsorption. LVs for ORR on a rotating Au(poly) electrode in oxygen saturated pure 0.1 M $HClO_4$ solution and in ones with the addition of the same acetonitrile concentrations as above, obtained for the same rotation rate of 1600 rpm are presented in Figure 6 (b). Detailed analysis of the kinetics of ORR on rotating Au single crystal disc – Pt ring electrodes in acid solutions reported earlier [27] have shown that ORR occurs in the double layer potential region (on oxide free surface) with the exchange of 2e, and that the transfer of the first electron is the rate determining step.

Apparent inhibition of ORR with the addition of acetonitrile is indicative of its adsorption over a wide potential range. With the increase of acetonitrile concentration in the solution, the onset of ORR is significantly shifted to the more negative potential, while the reaction kinetics is significantly hindered. ORR is almost completely blocked for acetonitrile concentration of 1.0 M, indicating that in this particular case, acetonitrile adsorption achieves a saturation value. Like in the case of Pt(poly), one can assume that adsorbed AcN molecules block the Au surface sites, preventing thus the adsorption of oxygen molecules and their subsequent oxidation.

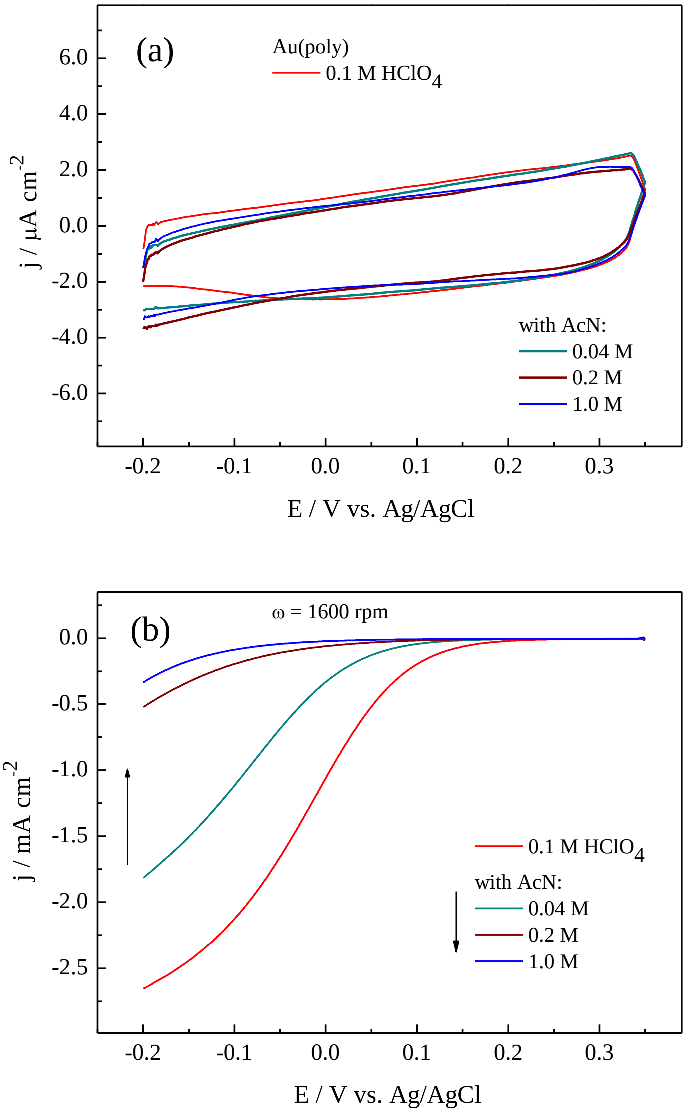


Figure 6. (a) CVs for a Au(poly) electrode recorded in oxygen free 0.1 M $HClO_4$ solution without and with the addition of 4.0 mM, 0.2 M and 1 M of acetonitrile; (b) LVs for ORR obtained for the same rotation rate of 1600 rpm on a rotating Au(poly) electrode in the same oxygen saturated solutions. Potential scan rate was 50 mV/s.

4. CONCLUSIONS

On the basis of the presented results regarding the effect of acetonitrile adsorption on oxygen reduction reaction on polycrystalline Pt and Au in perchlorate solutions, the following conclusions can be made.

Acetonitrile adsorbs on the Pt(poly) surface in a wide potential range and competes with the adsorption of hydrogen and OH anions. Both hydrogen and OH adsorption peaks are being increasingly suppressed, while the double layer expands for the lowest AcN concentration and than narrows with further increase of AcN concentration.

Adsorbed AcN occupy Pt surface sites thus preventing the adsorption of oxygen and its reduction. Acetonitrile adsorbs also on Au(poly), but compared to Pt(poly) it is not that evident, since there is no hydrogen adsorption on the initial surface. On the other hand, the inhibiting effect of AcN on the kinetics of ORR on Au(poly) is also very pronounced.

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